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New applications of carbon black. An aerogel-like composite material with heat insulating properties

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Abstract

A macroporous low-density aerogel-like composite material based on carbon black and polyvinyl alcohol has been developed. The structure and physicochemical properties of the material as well as the technique used for its synthesis are reported. The material is recommended for use as a heat insulator.

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1. Introduction

Carbon black is a highly disperse product of thermal-oxidative or thermal decomposition of hydrocarbons and has long been used in paint and varnish industry, printing industry, as a filler of various mechanical rubber goods and tires. A new direction in carbon black application is the synthesis of cryogel composites with high elasticity and hydrophobicity, which are recommended as constructional materials that can be used under severe conditions of Far North [1]. Another promising direction is the development of low-density aerogel-like materials based on carbon black, which, depending on their structure and properties, can find application as heat insulators, chemical sources of energy or catalyst supports.

According to the literature, carbon black [2], along with carbon nanotubes [3] or graphene [4], can be used to create composite aerogel materials with quite a low density (below 200 kg/m³). Such materials possess various structures and radically different physicochemical properties, which are determined by the composition of a gel precursor and by the methods of its synthesis and drying. In some cases, there are quite ordered structures of the

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house of cards [5] or cellular type [6], in other cases the structures are chaotic: filamentary [3] or cross-linked [5]. Microporous structures are formed only upon supercritical drying of composites [2], whereas freeze drying [4] or normal conditions [7] always lead to the formation of larger pores with less uniform sizes.

Hydrophobic composite aerogels with hierarchical meso- and macro-porosity are recommended as adsorbents of organics and heavy metals for wastewater treatment [6], conductive materials for chemical sources of energy [8], and heat-resistant composite aerogels for catalyst supports [9]. The known aerogel material consisting of carbon black and polyisocyanate can be employed as a heat insulator after drying in flowing CO₂ under supercritical conditions [2].

Our earlier works were devoted to modification of carbon black for its introduction into a gel precursor and exploration of conditions for the synthesis of composite aerogel-like materials containing carbon black and polyvinyl alcohol [10,11]. However, the acquired data were not systematic, the structure and properties of the synthesized material were not thoroughly studied. The goal of this work was to synthesize a composite aerogel-like material with good heat insulating properties and to make a comprehensive study of its properties.

2. Study subject

The study was performed with a composite aerogel-like material polyvinyl alcohol/carbon black that was synthesized by foaming of aqueous solutions of polyvinyl alcohol containing carbon black and OP-10 with subsequent two freeze-thaw cycles and drying of the resulting foam at room temperature according to the technique reported in [10]. The synthesis was carried out using two grades of polyvinyl alcohol (PVA), 99 % hydrolyzed and having different molecular weight: Sandiol 1399M (MW = 75000) and Sandiol 1799M (MW = 150000), and two samples of P 399-E grade carbon black: initial with the bulk density 220 kg/m³ and specific surface area 716 m²/g, and modified in flowing CO₂ at 1000 °C with the bulk density 92 kg/m³ and specific surface area 1285 m²/g [11]. Concentration of carbon black was 0.1% wt.; concentration of polyvinyl alcohol, 10% wt.; and pH of the medium, 7.

3. Methods

Density of dry samples was calculated from their volume to weight ratio according to the GOST 12730.1-78 method. The pore structure of composite aerogel-like materials was examined on a JSM-6610LV (JEOL, Japan) scanning electron microscope. Thermal stability of the samples was measured on a DTG-60H (Shimadzu, Japan) differential thermal analyzer in an argon flow (70 ml/min) upon heating at a rate of 10 °C/min. Total specific surface area (NSA) of the samples was determined from the low-temperature nitrogen adsorption on a Gemini 2380 analyzer according to the ASTM D 6556-10 technique. The average thermal conductivity coefficient of materials was calculated by a comparison of heat flows passing through the test sample, according to the instruction to an ITEM-1 thermal conductivity analyzer and using at least three measurements.

4. Results and discussion

A series of composite aerogel-like materials polyvinyl alcohol/carbon black was synthesized by cryogenic formation of the composite under its saturation by gas. A comprehensive study of the synthesized materials was made.

All the materials (Fig. 1) have a chaotic cross-linked structure. Its pore size does not exceed 650 μm, which is caused by the size of foaming gas bubbles, and increases with the molecular weight of PVA, whereas the size of pores in macropore walls varies from 0.5 μm to 10 μm and does not depend on the composition of precursor.

Mean pore size of aerogel

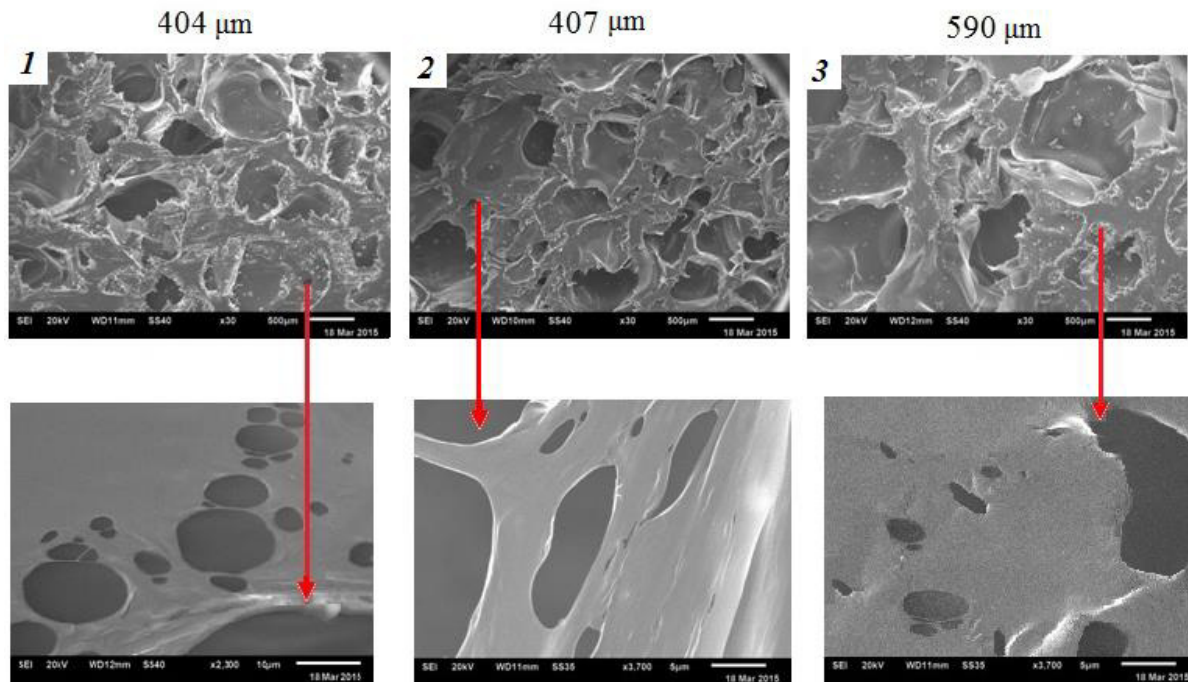


Fig. 1. SEM images of the structure of composite aerogel-like material polyvinyl alcohol/carbon black (1, 2 – MW = 75000; 3 – MW = 150000) at different magnification.

All the materials under consideration (Table 1) have approximately equal thermal stability of 260-280 °C, which does not depend on their composition and is determined by thermal stability of the matrix polymer, PVA.

Table 1. Thermal conductivity measurements of composite aerogel-like materials polyvinyl alcohol/carbon black.

Heat insulating material	Thermal conductivity coefficient (λ), W/m·K	Thermal stability not lower than (T), °C
Aerogel PVA 1399M/carbon black P 399-E	0.059	279
Aerogel PVA 1399M/mod. carbon black P 399-E	0.041	270
Aerogel PVA 1799M/mod. carbon black P 399-E	0.040	272
Aerogel PVA 1799M/mod. carbon black P 399-E	0.033	264
Aerogel polyisocyanate/carbon black [2]	0.019	-
Foamed polyurethane [12]	0.020-0.041	160
Foamed polystyrene [13]	0.031-0.050	70
Mineral wool [14]	0.038-0.120	300

Specific surface area of the synthesized materials strongly varied and depended on both the macropore size and specific surface area of carbon black (Fig. 2). The growth of specific surface area of carbon black increased the specific surface area of the corresponding aerogel-like materials, which reached 6 m²/g at a constant size of macropores in the composite. An increase in the macropore size of the composite considerably decreased its specific surface area in the presence of same carbon black, from 6 to 0.25 m²/g.

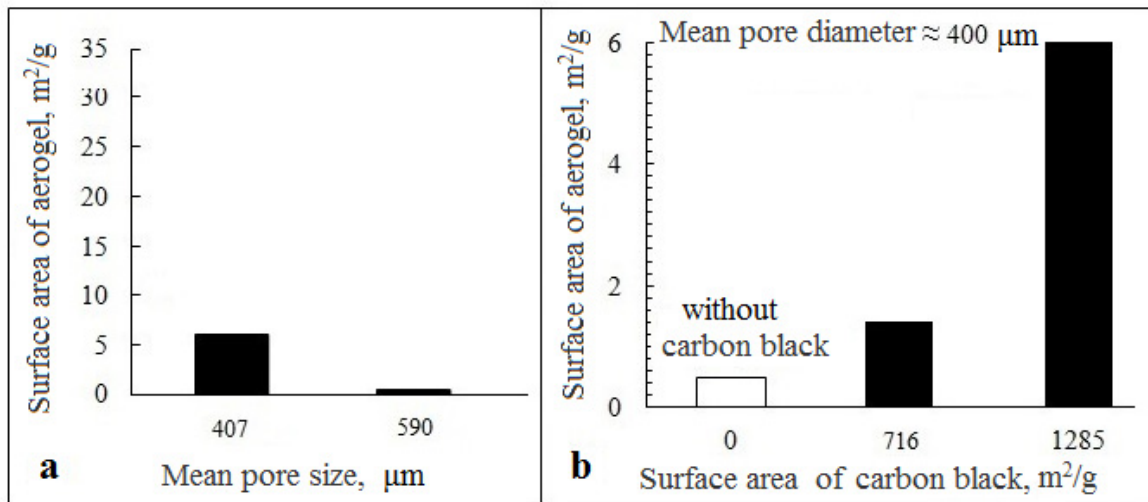


Fig. 2. Dependence of specific surface area of the composite aerogel-like material polyvinyl alcohol/carbon black (a) on the size of macropores (modified carbon black as a filler) and (b) on the specific surface area of carbon black at a similar macropore size.

Thermal conductivity measurements of thin sections of composite aerogel-like materials polyvinyl alcohol/carbon black showed that all the materials have approximately similar good heat insulating properties, with thermal conductivity coefficients of the materials correlating with their density (Fig. 3).

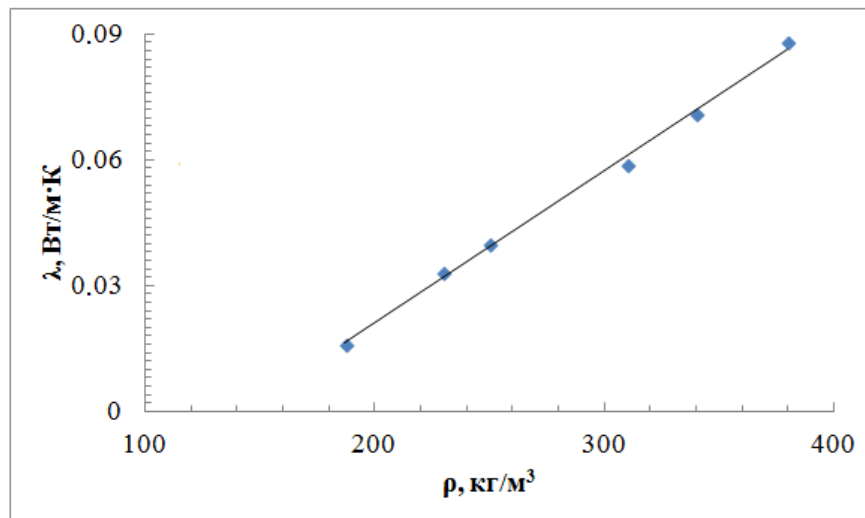


Fig. 3. Thermal conductivity coefficients (λ , $\text{W/m}\cdot\text{K}$) of composite aerogel-like materials polyvinyl alcohol/carbon black versus their density (ρ , kg/m^3).

The comparison of the materials synthesized in our work (Table 1) with the widely employed heat insulators demonstrated that composite aerogel-like materials polyvinyl alcohol/carbon black can compete with the known analogs.

5. Conclusion

Foaming of an aqueous solution of polyvinyl alcohol containing carbon black with subsequent freeze-thaw cycles and room temperature drying of the resulting foam were used to synthesize the macroporous aerogel-like material with specific surface area of 6 m²/g, heat resistance not lower than 260 °C, and good heat insulating properties.

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